

Iron K-Edge Xanes Study of Heated Green Beryl from Madagascar

Chawalit CHANKHANTHA^{1,*}, Panjawan THANASUTHIPITAK² and Pinit KIDKHUNTHOD³

¹Gems and Jewelry Industrial Development Section, Department of Industrial Promotion, Ministry of Industry, Bangkok 10110, Thailand

²Gemmology Program, Department of Geological Sciences, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

³Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima 30000, Thailand

(*Corresponding author's e-mail: charles.valydtth@gmail.com)

Presented at 41st Congress on Science and Technology of Thailand: November 6th - 8th 2015

Full paper accepted: 3 March 2016

Abstract

Rough green beryls from Madagascar were studied for their gemological characteristics after heat treatment. The conversion of the iron oxidation state after heating was studied using the modern technique of X-ray absorption spectroscopy. The X-ray absorption near edge spectroscopy (XANES) results are in conclusively agreement with the traditional Ultraviolet-visible-near infrared (UV-Vis-NIR) technique, where Fe³⁺ in an octahedral site is changed into Fe²⁺ after heat treatment. The undesirable yellow tinge in the stone, therefore, is expelled and, thus, an attractive blue color is developed. The green beryls contained moderate amounts of chromophore iron (up to 1.08 wt.% FeO_(total)), and relatively low amounts of Cs and Na. Fourier transform infrared (FTIR) spectroscopic features and chemical analyses are consistent with alkali-poor beryl. The gemological characterization of Malagasy green beryl is also presented in detail.

Keywords: Beryl, heat treatment, UV-Vis-NIR, FTIR, XANES

Introduction

Green beryl is a pastel-green gemstone from the colorful group of beryls, with an ideal composition of Be₃Al₂Si₆O₁₈, better known as emerald, the most expensive beryl. The structure of beryl belongs to a space group of *P6/mmc*, with lattice parameters $a = 9.221 \text{ \AA}$ and $c = 9.186 \text{ \AA}$ [1]. It consists of [Si₆O₁₈]¹²⁻ hexagonal rings lying in a plane parallel to the *c*-axis. These rings are linked together both laterally and vertically by Be²⁺ in a tetrahedral site and Al³⁺ in an octahedral site, forming a 3-dimensional framework and vertical structural channel sites (**Figures 1a** and **1b**). The large channel sites can host various molecules (*e.g.*, H₂O, CO₂, CH₄ and NO₃), and alkali ions (*e.g.*, Na⁺, K⁺, Rb⁺ and Cs⁺) [2]. The color of beryl depends upon the structural substitution caused by various impurities (*e.g.*, V, Cr, Mn or Fe). The light to medium green color of beryl generally results from either V³⁺ or is generated from the mixture of yellow from an octahedral Fe³⁺, and blue from an Fe²⁺ in the channel site [3,4]. Water molecules within the channel site can be classified into two types; type-I water is not connected with alkali ions, whereas type-II water is associated with alkali ions [5].

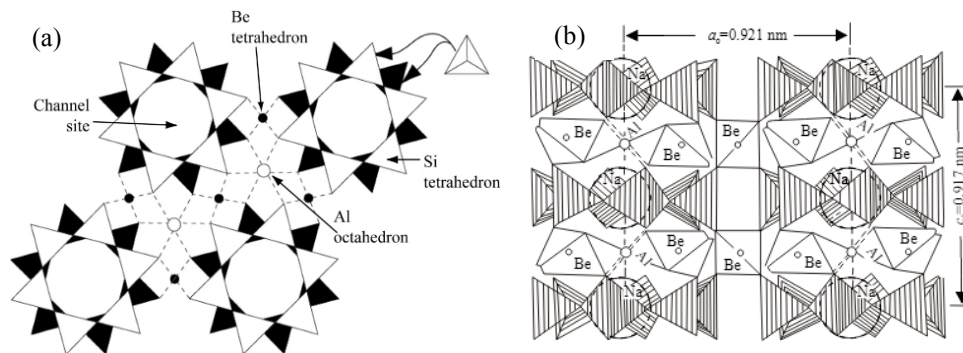


Figure 1 (a) Crystal structure of beryl projected on basal plane (0001) [4], and (b) Crystal structure of beryl in direction perpendicular to *c*-axis [6].

Green beryl is usually an accessory mineral, occurring mainly in beryllium-rich granitic pegmatite, and partly in some highly diffracted granite or metamorphic rocks. It is commonly formed as small to large prismatic and tabular shapes in pockets. Pegmatite-related deposits in Madagascar are related to the Pan-African Mozambique belt (570 - 540 Ma) which resulted from the collision between the East and West of Gondwana. This geologic event generated a lot of magmatic fluid and led to the formation of a wide variety of different types of pegmatites. Beryl deposits in Madagascar have been commercially produced from several mines in the Betafo-Antsirabe region of the Antananarivo province, which is underlain by migmatite of the Precambrian crystalline basement of central Madagascar (Antananarivo Block). The Malagasy gem beryl-bearing pegmatites are classified as a rare-element LCT (lithium, cesium, and tantalum) type body of the beryl-columbite subtype [7,8].

Many investigators have previously reported about the role of iron atoms in beryl, using various sophisticated instruments including Ultraviolet-visible-near infrared (UV-Vis-NIR), Mössbauer, LIBS, and Electron paramagnetic resonance (EPR) spectroscopy [9-12]. However, there has been no conclusive proof offered about this role. In an effort to resolve this, green beryls samples are here studied, using an X-ray absorption spectroscopy, in order to reveal the valence states of Fe atoms in beryl.

Materials and methods

Thirty-five rough green beryls (1.31 - 4.56 cts) from Madagascar were characterized and heat treated in this study. The samples ranged from light green to medium yellowish green. All samples were examined using standard gemological instruments to determine their hydrostatic specific gravity, refractive indices, and UV fluorescence. Internal characteristics were examined with a gemological microscope. UV-Vis-NIR absorption spectra were recorded over an interval of 300 - 1000 nm using a Hitachi U4001 spectrophotometer, with a slit width of 2 mm and a scan speed of 300 nm/min. Infrared spectra were collected using a Bruker Tensor 27 FTIR spectrometer, with a standard resolution of 4 cm^{-1} and 120 scans per sample. Quantitative chemical analyses were performed on ten samples using a JEOL (JXA-8100) electron microprobe in wavelength-dispersive mode. The results were automatically corrected by a ZAF correction procedure. X-ray absorption near-edge spectra (XANES) were recorded at BL-8 of the Synchrotron Light Research Institute (SLRI), Thailand. The instrument was equipped with a Ge (220) double crystal monochromator calibrated at the inflexion point of the absorption edge for iron (7112 eV), and was taken at the Fe *K*-edge in fluorescence yield mode by using a 13-element Ge detector. Iron standard spectra (FeO and Fe₂O₃ for Fe²⁺ and Fe³⁺, respectively) were used as references of the edge position in the various valence states. All XANES spectra were extracted from the ATHENA program which is included in an IFEFFIT package [13,14]. Heat treatment experiments were carried out using an electrical furnace with a programmable controller at the Department of Geological Sciences, Chiang Mai University. The reducing atmosphere was created by purging an inert argon gas into the heating chamber

to minimize the level of oxygen during the heating process. All samples were heated twice in accordance with the stipulated temperatures of 350 and 400 °C, with a soaking time of one hour.

Results and discussion

Gemological testing gave a specific gravity of 2.66 - 2.72, and refractive indices were $n_o = 1.566 - 1.581$, and $n_e = 1.560 - 1.575$, yielding a birefringence of 0.006 - 0.008. All samples were inert to both long- and short-wave UV radiation. These properties are consistent with beryl in general. Microscopic examination revealed fractures with iron stains, partially healed fractures with fluid and 2-phase, iridescent thin-film fluid, parallel growth tubes, negative crystals, and mineral inclusions. The UV-Vis-NIR absorption spectra (**Figure 3**) were typical for aquamarine, with a general 2 peaks at 370 and 427 nm due to octahedral Fe^{3+} , and a strong broad band centered at around 820 nm was assigned to either Fe^{2+} in octahedral sites or to structural channel sites [4,5,12,15,16]. The heating experiments showed that the optimum heating temperature for enhancing the color of the stones is at 400 °C. After heating, the intensity of the Fe^{3+} absorption band decreased slightly, resulting from the change of the valence state of the iron from Fe^{3+} to Fe^{2+} . Therefore, the unfavorable yellow overcast in the stones were eradicated, hence making the samples come to be an attractive blue (**Figure 2**).

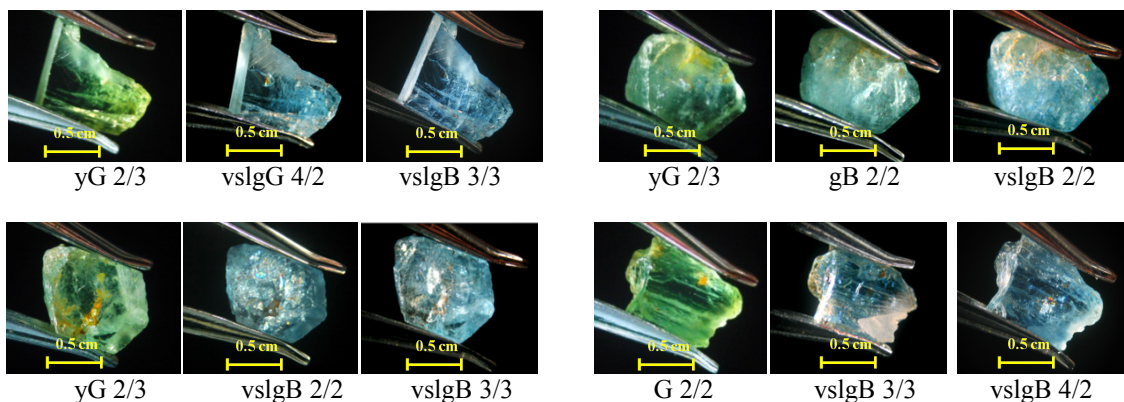


Figure 2 Color comparison of green beryl samples before and after heat treatment at 350 and 400 °C, respectively, under reducing atmosphere (GIA Gem Set codes are described to compare the change of coloration).

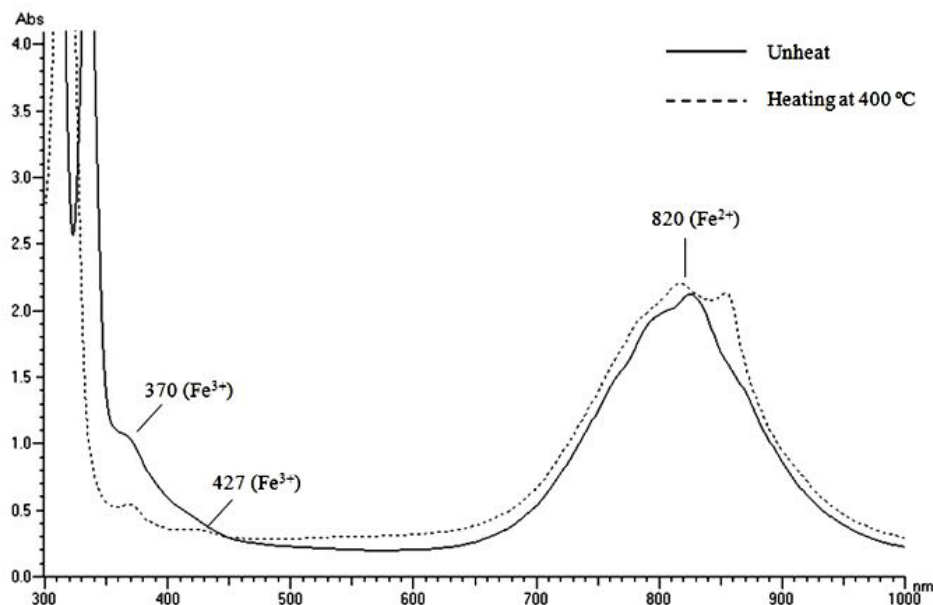


Figure 3 UV-Vis-NIR absorption spectra of green beryl (sample_025), in the direction of the o-ray (E⊥c), showing the decrease of Fe³⁺ peaks after heat treatment.

Electron-microprobe analyses of 5 green beryl samples showed rather low Fe contents, varying from 0.21 to 1.08 wt.% FeO_(total), compared to those of similar green-blue beryls from the Yukon Territory, Canada, up to 5.04 wt.% FeO_(total) [17], 1.37 - 1.50 wt.% FeO_(total) in Vietnamese beryls [18], and 0.46 - 0.47 wt.% FeO_(total) in Italian beryls [19]. Cs₂O contents of all samples were below the detection limit, and sodium values ranged from 0.25 to 0.56 wt.% Na₂O. According to the classification of beryl [20], these Malagasy green beryls can be classified as alkali-poor beryl.

FTIR spectra of green beryl (**Figure 4**) showed broad bands due to type-I and type-II water molecules between 4000 and 3400 cm⁻¹. The band at 2360 cm⁻¹ indicated the presence of CO₂. A doublet band displayed at 3206 and 3110 cm⁻¹ can be assigned to either type-II water or to hydroxide oriented parallel to the *c*-axis. The near infrared region revealed peaks of type-I water at 5455 and 5106 cm⁻¹, whereas a weak band at 5272 cm⁻¹ was related to type-II water [5,21]. The low intensity of both type-I and type-II water, in general, indicates a much lesser amount of alkali ions, with yields consistent with alkali-poor beryl.

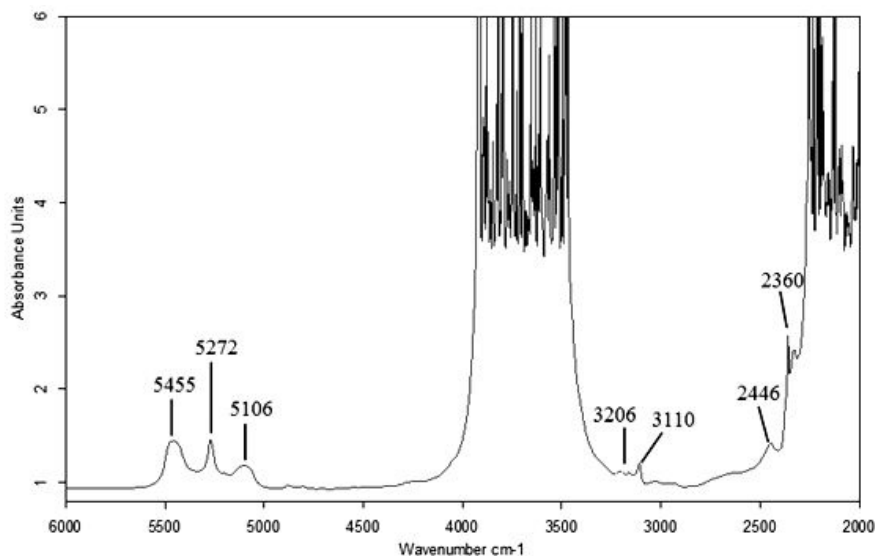


Figure 4 Infrared spectrum of unheated Malagasy green beryl, displaying the vibrational absorption bands due to H₂O, CO₂ and (OH)⁻.

In this study, X-ray absorption spectroscopy was mainly used to probe the oxidation state and structural state of iron. XANES spectra of green beryls were measured at Fe *K*-edge (**Figure 5**). It was clearly shown that unheated spectra obviously overlapped to the Fe₂O₃ reference sample at 7125 eV. After heating at 400 °C under reducing conditions, the spectra were shifted into a lower energy at 7120 eV, matching the FeO reference sample. This is a strong indication that the octahedral Fe³⁺ was converted into Fe²⁺ after heating under reducing conditions. The pre-edge peak at around 7115 eV was not identified.

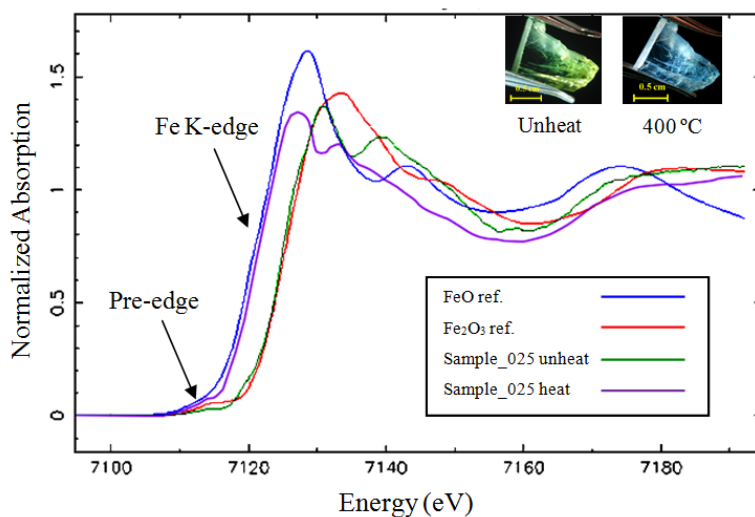


Figure 5 Fe *K*-edge XANES spectra of unheated green beryls (green line) and after heating at 400 °C (purple line), compared with Fe₂O₃ (red line), and FeO reference spectra (blue line).

Conclusions

The gemological properties of green beryls from Madagascar are similar to those gem beryls from other localities. Based on chemical analyses, they are classified as alkali-poor beryl. Heat treatment at 400 °C under a reducing atmosphere can change the unfavorable green color into an attractive blue, which is more expensive, having long been known as aquamarine in the trade. The blue color in heated beryls is attributed to the conversion of yellow-causing octahedral Fe³⁺ to colorless Fe²⁺, which is conclusively proven by XANES and UV-Vis-NIR spectroscopy.

Acknowledgements

The authors are grateful to the Thai Research Fund (TRF) and the Thai Gem and Jewelry Traders Association (TGJTA) for financial support. X-ray absorption spectroscopy was provided by the Synchrotron Light Research Institute (Thailand). EPMA analyses were performed at the Department of Geology, Chulalongkorn University, Thailand.

References

- [1] WL Bragg and J West. The structure of beryl, Be₃Al₂Si₆O₁₈. *Proc. Roy. Soc.* 1926; **111**, 691-713.
- [2] C Aurisicchio, O Grubessi and P Zecchini. Infrared spectroscopy and crystal chemistry of the beryl group. *Can. Miner.* 1994; **32**, 55-68.
- [3] DS Goldman, GR Rossman and KM Parkin. Channel constituents in beryl. *Phys. Chem. Miner.* 1978; **3**, 225-35.
- [4] RR Viana, H Jordt-Evangelista, GM de Costa and WB Stern. Characterization of beryl (aquamarine variety) from pegmatites of Minas Gerais, Brazil. *Phys. Chem. Miner.* 2002; **29**, 668-79.
- [5] DL Wood and K Nassau. The characterization of beryl and emerald by visible and infrared absorption spectroscopy. *Am. Miner.* 1968; **53**, 777-800.
- [6] L Yan, D Jun, L Guowu and S Guanghai. Structure refinement of Cs-rich Na-Li beryl and analysis of its typomorphic characteristics of configurations. *Acta Geol. Sinica* 2007; **81**, 61-7.
- [7] A Lacroix. *Minéralogie de Madagascar, Tome II, Appliquée, Lithologie*. Augustin Challamel, Paris, 1922.
- [8] F Pezzotta. *Madagascar, A Mineral and Gemstone Paradise, ExtraLapis English 1*. Lapis International LLC, East Hampton, CT USA, 2001.
- [9] AR Blak, S Isotani and S Watanabe. Optical absorption and electron spin resonance in blue and green natural beryl. *Phys. Chem. Miner.* 1982; **8**, 161-6.
- [10] G Mathew, RV Karanth, TKG Rao and RS Deshpande. Colouration in natural beryls: A spectroscopy investigation. *Curr. Sci. India* 1997; **73**, 1004-11.
- [11] CE McManus, NJ McMillan, RS Harmon, RC Whitmore, FC DeLucia and AW Miziolek. Use of laser induced breakdown spectroscopy in the determination of gem provenance: Beryls. *Appl. Optics* 2008; **47**, 72-9.
- [12] DC Price, ER Vance, G Smith, A Edgar and BL Dickson. Mössbauer effect studies of beryl. *J. Phys.* 1976; **37**, 811-7.
- [13] M Newville. IFEFFIT: Interactive XAFS analysis and FEFF fitting. *Synchrotron Rad.* 2001; **8**, 322-4.
- [14] B Ravel and MJ Newville. ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT. *Synchrotron Rad.* 2005; **12**, 537-41.
- [15] G Spinolo, I Fontana and A Galli. Optical absorption spectra of Fe²⁺ and Fe³⁺ in beryl crystals. *Phys. Status Solidi B* 2007; **244**, 4360-8.
- [16] MN Taran and GR Rossman. Optical spectroscopy of tuzovite and a re-examination of the beryl, cordierite, and osumilite spectra. *Am. Miner.* 2001; **86**, 973-80.
- [17] I Adamo, A Pavese, L Prospero, V Diella, D Ajò, GD Gatta and CP Smith. Aquamarine, Maxixe-type beryl, and hydrothermal synthetic blue beryl: Analysis and identification. *Gems Gemol.* 2008; **44**, 214-26.

- [18] LTT Huong, W Hofmeister, T Häger, NN Khoi, NT Nhung, W Atichat and V Pisuta-Arnond. Aquamarine from the Thuong Xuan district, Thanh Hoa province, Vietnam. *Gems Gemol.* 2011; **47**, 42-8.
- [19] R Bocchio, I Adamo and F Caucia. Aquamarine from the Masino-Bregaglia Massif, Central Alps, Italy. *Gems Gemol.* 2009; **45**, 204-7.
- [20] FC Hawthorne and P Černý. The alkali-metal positions in Cs-Li beryl. *Can. Miner.* 1977; **15**, 414-21.
- [21] JC Zwaan, DE Jacob, T Häger, MTOC Neto and J Kanis. Emeralds from the Fazenda Bonfim region, Rio Grande do Norte, Brazil. *Gems Gemol.* 2012; **48**, 2-17.